

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2003-323822

(43)Date of publication of application : 14.11.2003

(51)Int.Cl.

H01B 12/06  
H01B 13/00  
// G23C 14/06

(21)Application number : 2002-130623

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(22)Date of filing : 02.05.2002

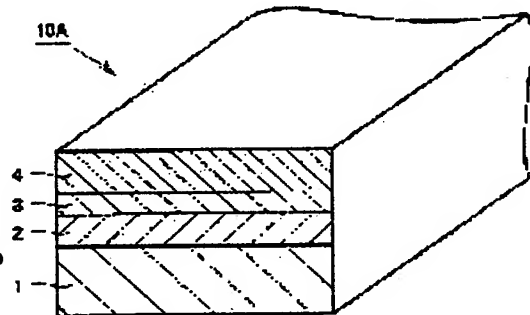
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## (54) THIN-FILM SUPERCONDUCTIVE WIRE MATERIAL AND PRODUCTION PROCESS THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a thin-film superconductive wire material having high critical current density in the construction that an RE123 superconductive layer is formed on a metal tape substrate, and a production process thereof.

SOLUTION: The production process of the thin-film superconductive wire material 10A comprises the steps of forming an intermediate layer 2 on a metal tape substrate 1, forming a first superconductive layer 3 having an RE123 composition as a diffusion-preventing layer on the intermediate layer 2 and forming a second superconductive layer 4 having an RE123 composition so as to come into contact with the first superconductive layer 3.



## LEGAL STATUS

[Date of request for examination]

24.12.2004

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

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## CLAIMS

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[Claim(s)]

[Claim 1] The manufacture approach of the thin film superconduction wire rod equipped with the process which forms the 1st superconduction layer which has the presentation of RE123 system on a metal tape substrate, and the process which forms the 2nd superconduction layer which has the presentation of RE123 system so that said 1st superconduction layer may be touched.

[Claim 2] The manufacture approach of the thin film superconduction wire rod according to claim 1 characterized by having further the process which forms an interlayer between said metal tape substrate and said 1st superconduction layer.

[Claim 3] The temperature at the time of membrane formation of said 2nd superconduction layer is the manufacture approach of the thin film superconduction wire rod according to claim 1 or 2 characterized by being higher than the temperature at the time of membrane formation of said 1st superconduction layer.

[Claim 4] The oxygen tension at the time of membrane formation of said 2nd superconduction layer is the manufacture approach of the thin film superconduction wire rod according to claim 3 characterized by being higher than the oxygen tension at the time of membrane formation of said 1st superconduction layer.

[Claim 5] The thin film superconduction wire rod equipped with the 2nd superconduction layer which does not contain the component which is formed so that the 1st superconduction layer containing the component which is formed on a metal tape substrate and said metal tape substrate, has the presentation of RE123 system, and is contained in the construction material of a substrate, and said 1st superconduction layer may be touched, and has the presentation of RE123 system, and is contained in the construction material of said substrate.

[Claim 6] The thin film superconduction wire rod according to claim 5 characterized by having further the interlayer formed between said metal tape substrate and said 1st superconduction layer.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention relates to the thin film superconduction wire rod with which the superconduction layer which has the presentation of RE123 system was formed on the metal tape substrate, and its manufacture approach about a thin film superconduction wire rod and its manufacture approach.

[0002]

[Description of the Prior Art] When forming a superconduction thin film of RE123 system like the presentation of RE1 B-2C 3O7 on a single crystal substrate, high critical current density ( $J_c$ ) is obtained, but when forming on a metal tape substrate, high critical current density is difficult to get. this -- a single crystal -- a substrate -- a case -- \*\*\*\* -- aluminum -- two -- O -- three -- LaAlO -- three -- MgO -- etc. -- an oxide -- a substrate -- using -- having -- a sake -- a substrate -- superconduction -- a thin film -- diffusion -- a reaction -- being generated -- being hard -- although -- a metal -- a tape -- a substrate -- a case -- \*\*\*\* -- a metal -- a tape -- a substrate -- using -- having -- stainless steel -- nickel -- (-- nickel --) -- an alloy -- silver -- (-- Ag --) -- an alloy -- etc. -- superconduction -- a thin film -- diffusion -- a reaction -- be generated -- since -- it is .

[0003] In addition, in the above ""RE"" of RE1 B-2C3O7"" is ""B about rare earth elements (for example, yttrium)"" , ""C"" means copper (Cu) and ""O"" means oxygen (O) for barium (Ba).

[0004] Moreover, junction between crystal grain also becomes firm, and the compactness of the crystal of RE123 system can attain the high critical current density  $J_c$ , so that the temperature at the time of membrane formation by the gaseous-phase method (laser vacuum deposition, a spatter, electron beam method) is high. However, as for a metal tape substrate, the diffusion reaction of a substrate and a superconduction thin film serves as activity at an elevated temperature for a metal. For this reason, generally by the gaseous-phase method, temperature at the time of membrane formation was not able to be made into the elevated temperature.

[0005]

[Problem(s) to be Solved by the Invention] In order to prevent the above-mentioned diffusion reaction, interlayers, such as cerium oxide (CeO<sub>2</sub>) and yttria stabilized zirconia (YSZ), are formed between a metal tape and a superconduction layer.

[0006] However, since an interlayer's selenium (Ce), an yttrium (Y), etc. react with the superconduction layer of RE123 system, even if it prepares an interlayer, high critical current density  $J_c$  like [ in the case of forming a superconduction layer on a single crystal substrate ] is not obtained.

[0007] So, the object of this invention is offering the thin film superconduction wire rod which has high critical current density in the configuration which forms the superconduction layer of RE123 system on a metal tape substrate, and its manufacture approach.

[0008]

[Means for Solving the Problem] The manufacture approach of the thin film superconduction wire rod of this invention is equipped with the process which forms the 1st superconduction layer which has the presentation of RE123 system on a metal tape substrate, and the process which forms the 2nd superconduction layer which has the presentation of RE123 system so that the 1st superconduction layer may be touched.

[0009] According to the manufacture approach of the thin film superconduction wire rod of this invention, since the 1st superconduction layer turns into a diffusion prevention layer, it can prevent that the metallic element of a metal tape substrate is spread in the 2nd superconduction layer. It can prevent by this that the 2nd superconduction layer carries out a diffusion reaction with a metal tape substrate, and high critical current density can be obtained.

[0010] Moreover, since the 1st superconduction layer used as a diffusion prevention layer turns into the 2nd superconduction layer from the same construction material substantially, a diffusion

reaction does not arise between the 1st superconduction layer and the 2nd superconduction layer.

[0011] In addition, "RE123 system" in this application description means that it is  $0.7 \leq x \leq 1.3$ ,  $1.7 \leq y \leq 2.3$ , and  $2.7 \leq z \leq 3.3$  in  $\text{RE}_x\text{Ba}_y\text{Cu}_z\text{O}_{7-d}$ . Moreover, RE of "RE123 system" means the construction material of rare earth elements and an yttrium element which contains either at least. Moreover, as rare earth elements, neodymium (Nd), a gadolinium (Gd), HORMINIUM (Ho), samarium (Sm), etc. are contained, for example.

[0012] In the manufacture approach of the above-mentioned thin film superconduction wire rod, it has further preferably the process which forms an interlayer between a metal tape substrate and the 1st superconduction layer.

[0013] Thus, since the 1st superconduction layer functions as a diffusion prevention layer even when an interlayer is prepared, it can prevent that the 2nd superconduction layer carries out a diffusion reaction with an interlayer, and high critical current density can be obtained.

[0014] In the manufacture approach of the above-mentioned thin film superconduction wire rod, the temperature at the time of membrane formation of the 2nd superconduction layer is higher than the temperature at the time of membrane formation of the 1st superconduction layer preferably.

[0015] By making low temperature at the time of membrane formation of the 1st superconduction layer, it can control that the 1st superconduction layer carries out a diffusion reaction with the substrate of a metal tape etc. Moreover, by making high temperature at the time of membrane formation of the 2nd superconduction layer, it improves, junction between crystal grain also becomes firm, and the compactness of the crystal of the 2nd superconduction layer of RE123 system can attain the high critical current density  $J_c$ . Thus, by controlling the temperature at the time of membrane formation of each class, the thin film superconduction wire rod which is a diffusion reaction and which has a critical high current value while being able to control can be obtained.

[0016] In the manufacture approach of the above-mentioned thin film superconduction wire rod, the oxygen tension at the time of membrane formation of the 2nd superconduction layer is higher than the oxygen tension at the time of membrane formation of the 1st superconduction layer preferably.

[0017] Usually, in the superconduction layer of RE123 system, since the melting point of a superconduction layer will become high if the oxygen tension at the time of membrane formation becomes high, it becomes possible to make temperature at the time of membrane formation into an elevated temperature. Since this is enabled to form the 2nd superconduction layer at an elevated temperature rather than the 1st superconduction layer, as mentioned above, the compactness of the crystal of the 2nd superconduction layer improves, junction between crystal grain also becomes firm, and the high critical current density  $J_c$  can be attained.

[0018] The thin film superconduction wire rod of this invention is equipped with a metal tape substrate, the 1st superconduction layer, and the 2nd superconduction layer. The 1st superconduction layer contains the component which is formed on a metal tape substrate, has the presentation of RE123 system, and is contained in the construction material of a substrate. The 2nd superconduction layer does not contain the component which is formed so that the 1st superconduction layer may be touched, and has the presentation of RE123 system, and is contained in the construction material of a substrate.

[0019] According to the thin film superconduction wire rod of this invention, since the 1st superconduction layer turns into a diffusion prevention layer, it can prevent that the metallic element of a metal tape substrate is spread in the 2nd superconduction layer. It can prevent by this that the 2nd superconduction layer carries out a diffusion reaction with a metal tape substrate, and high critical current density can be obtained.

[0020] Moreover, since the 1st superconduction layer used as a diffusion prevention layer turns into the 2nd superconduction layer from the same construction material substantially, a diffusion reaction does not arise between the 1st superconduction layer and the 2nd superconduction layer.

[0021] In the above-mentioned thin film superconduction wire rod, it has further preferably the

interlayer formed between a metal tape substrate and the 1st superconduction layer.

[0022] Thus, since the 1st superconduction layer functions as a diffusion prevention layer even when an interlayer is prepared, it can prevent that the 2nd superconduction layer carries out a diffusion reaction with an interlayer, and high critical current density can be obtained.

[0023]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained based on drawing.

[0024] Drawing 1 is the partial cross-section perspective view showing roughly the configuration of the thin film superconduction wire rod in the gestalt of 1 operation of this invention. With reference to drawing 1, the thin film superconduction wire rod 10 in the gestalt of this operation has the metal tape substrate 1, an interlayer 2, the 1st superconduction layer 3, and the 2nd superconduction layer 4.

[0025] The metal tape substrate 1 consists of construction material of stainless steel, a nickel alloy (for example, Hastelloy), a silver alloy, etc. An interlayer 2 is a diffusion prevention layer, for example, consists of construction material, such as cerium oxide, YSZ, magnesium oxide, an oxidization yttrium, an oxidization ytterbium, and a barium zirconia, and is formed on the metal tape substrate 1.

[0026] The 1st superconduction layer 3 is formed on the interlayer 2, including the component which has the presentation of RE123 system and is contained in the construction material of a substrate (interlayer 2). The 2nd superconduction layer 4 does not contain the component which is formed so that the 1st superconduction layer 3 may be touched, and has the presentation of RE123 system, and is contained in the construction material of a substrate (interlayer 2). The 1st and 2nd superconduction layers 3 and 4 consist of construction material of the same presentation substantially, for example, consist of Ho1 B-2C 3O7.

[0027] As shown in drawing 2, the conventional thin film superconduction wire rod 110 has the metal tape substrate 101, the interlayer 102, and the superconduction layer 103. As compared with this conventional configuration, a superconduction layer consists of two-layer [ of the 1st and 2nd superconduction layers 3 and 4 ], and, as for the configuration of the gestalt of this operation, the 1st superconduction layers 3 differ in the point (that is, it prevents that the metallic element in an interlayer 2 is spread in the 2nd superconduction layer 4) of functioning as a diffusion prevention layer. Thereby, by thin film superconduction wire rod 10A of the gestalt of this operation, an interlayer's 2 metallic element is not contained in the 2nd superconduction layer 4 to an interlayer's 102 metallic element having been contained in the superconduction layer 104 in the conventional thin film superconduction wire rod 110.

[0028] Although the configuration which formed the interlayer 2 in drawing 1 was explained, as shown in drawing 3, the interlayer was omitted, and the 1st superconduction layer 3 may be directly in contact with the front face of the metal tape substrate 1. In this configuration, since the 1st superconduction layer 3 functions as a diffusion prevention layer, the metallic element of the metal tape substrate 1 is not contained in the 2nd superconduction layer 4.

[0029] In addition, since the configuration of those other than this of thin film superconduction wire rod 10B shown in drawing 3 is almost the same as the configuration shown in drawing 1 mentioned above, the explanation is omitted.

[0030] Moreover, the interlayer 2 who shows drawing 1 may be omitted, and as shown in drawing 4, a metal tape substrate may be used as the compound tape substrate of the tape 1 which consists of stainless steel, and the tape 5 which consists of silver. Silver is the construction material which a diffusion reaction with a superconduction layer cannot produce easily rather than other metals. For this reason, even if it vapor-deposits the superconduction layers 3 and 4 at a direct elevated temperature on a silver larer 5, the property of the good critical current density Jc is acquired.

[0031] In addition, since the configuration of those other than this of thin film superconduction wire rod 10C shown in drawing 4 is almost the same as the configuration shown in drawing 1 mentioned above, it attaches the sign same about the same member, and omits the explanation.

[0032] Next, the manufacture approach of the thin film superconduction wire rod in the gestalt of this operation is explained. Drawing 5 is flow drawing showing the manufacture approach of the

thin film superconduction wire rod in the gestalt of 1 operation of this invention. the interlayer 2 who the metal tape substrate 1 is prepared (step S1), and consists of YSZ on this metal tape substrate 1 with reference to drawing 1 and drawing 5 by the manufacture approach of the thin film superconduction wire rod of the gestalt this operation — PLD (Pulsed Laser Deposition) — ISD (Inclined Substrate Deposition) by law (laser vacuum deposition) — it is formed of law (step S2). the 1st superconduction layer 3 which has the presentation (for example, Ho1 B-2C 307) of RE123 system on this interlayer 2 — for example, PLD — it is formed of law (step S3). the 2nd superconduction layer 4 which has the presentation (for example, Ho1 B-2C 307) of RE123 system on this 1st superconduction layer 3 — for example, PLD — it is formed of law (step S4) and thin film superconduction wire rod 10A is manufactured by performing after treatment.

[0033] In addition, when manufacturing thin film superconduction wire rod 10B shown in drawing 3, the above-mentioned interlayer's 2 formation process (step S2) is skipped. Moreover, when manufacturing thin film superconduction wire rod 10C shown in drawing 4, a metal tape substrate is prepared as a compound tape substrate of the tape 1 which consists of stainless steel, and the tape 5 which consists of silver, and an interlayer's 2 formation process (step S2) is skipped.

[0034] According to the gestalt of this operation, since the 1st superconduction layer 3 functions as a diffusion prevention layer, it can prevent that an interlayer's 2 (or metal tape substrate 1) metallic element is spread in the 2nd superconduction layer 4. It can prevent by this that the 2nd superconduction layer 4 carries out a diffusion reaction with an interlayer 2 (or metal tape substrate 1), and high critical current density can be obtained.

[0035] Moreover, since the 1st superconduction layer 3 used as a diffusion prevention layer turns into the 2nd superconduction layer 4 from the same construction material substantially, a diffusion reaction does not arise between the 1st superconduction layer 3 and the 2nd superconduction layer 4.

[0036] As for the temperature at the time of membrane formation of the 2nd superconduction layer 4, in the above-mentioned manufacture approach, it is desirable that it is higher than the temperature at the time of membrane formation of the 1st superconduction layer 3. Thus, by making low temperature at the time of membrane formation of the 1st superconduction layer 3, it can control that the 1st superconduction layer 3 carries out a diffusion reaction with an interlayer's 2 (or metal tape substrate 1) substrate. Moreover, by making high temperature at the time of membrane formation of the 2nd superconduction layer 4, it improves, junction between crystal grain also becomes firm, and the compactness of the crystal of the 2nd superconduction layer 4 of RE123 system can attain the high critical current density  $J_c$ . Thus, by controlling the temperature at the time of membrane formation of each class, thin film superconduction wire rod 10A (or 10B) which is a diffusion reaction and which has a critical high current value while being able to control can be obtained.

[0037] As for the oxygen tension at the time of membrane formation of the 2nd superconduction layer 4, in the above-mentioned manufacture approach, it is desirable that it is higher than the oxygen tension at the time of membrane formation of the 1st superconduction layer 3. Usually, in the superconduction layer of RE123 system, since the melting point of a superconduction layer will become high if the oxygen tension at the time of membrane formation becomes high, it becomes possible to make temperature at the time of membrane formation into an elevated temperature. Since this is enabled to form the 2nd superconduction layer 4 at an elevated temperature rather than the 1st superconduction layer 3, as mentioned above, the compactness of the crystal of the 2nd superconduction layer 4 improves, junction between crystal grain also becomes firm, and the high critical current density  $J_c$  can be attained.

[0038] Moreover, since the 1st superconduction layer 3 functions as a diffusion prevention layer, it becomes possible to take the long membrane formation time amount of the 2nd superconduction layer 4, and thick-film-ization (high [ $J_c$ ]) of the 2nd superconduction layer 4 is attained.

[0039] Moreover, when formed of the technique (Rabits (Rolling-Assisted Biaxially Textured Substrates) the ISD method and law) from which an interlayer 2 does not become comparatively precise, it becomes easy to diffuse a metallic element in a superconduction layer. For this



reason, a diffusion reaction can be more effectively prevented by combining the gestalt of this operation with such an interlayer.

[0040] Moreover, as for the 1st of RE123 system and the 2nd superconduction layer 3 and 4 in the gestalt of this operation, it is desirable that the stacking tendency within a field is all the c axis orientation film 20 degrees or less. Moreover, even if the 1st superconduction layer 3 which functions as a diffusion prevention layer has neither a gap of a presentation nor a certain specific element, it can play a role.

[0041]

[Example]

(Example 1) a nickel alloy tape (70 micrometers in Hastelloy, width-of-face [ of 10mm ], thickness) top — PLD — the YSZ interlayer with a thickness of 2 micrometers was formed by the ISD method using law (laser vacuum deposition). Although the nickel alloy tape was non-orientation, the YSZ interlayer had the biaxial orientation whose stacking tendency within a field is about 18 degrees according to the effectiveness of ISD. besides — 3OHo1 B-2C7 film — PLD — membranes were formed by the thickness of 1 micrometer by law. Membrane formation conditions are a part for 13.3Pa (=100mTorr) of oxygen tension, and oxygen flow rate of 300cm<sup>3</sup>/s(=300sccm), and laser output 50W (1Jx50Hz), and shook the heater temperature at the time of membrane formation by 10-degree-C unit from 900 degrees C to 1000 degrees C. Consequently, the film with the property (electrization Jc) of a maximum of 0.08 MA/cm<sup>2</sup> (77K, 0T) was obtained with the heater temperature of 920 degrees C. In the heater temperature of 960 degrees C, the critical current values Jc were 0.07 MA/cm<sup>2</sup>.

[0042] On the other hand, the 1st 3OHo1 B-2C7 1-micrometer film was formed with the heater temperature of 900 degrees C on the same conditions. Then, heater temperature was changed on the still more nearly same conditions with 920 degrees C, 940 degrees C, 960 degrees C, and 980 degrees C, and the 2nd 3OHo1 B-2C7 1-micrometer film was formed on it. Consequently, in the heater temperature of 960 degrees C, 3OHo1 B-2C7 film with the property (electrization Jc) of 0.3 MA/cm<sup>2</sup> (77K, 0T) was obtained.

[0043] As a result of observing by SEM (Scanning Electron Microscope), the 2nd 3OHo1 B-2C7 upper film was a very precise smooth film surface compared with the 1st 3OHo1 B-2C7 lower layer film.

[0044] (Example 2) The nickel alloy tape and YSZ interlayer who become a substrate were manufactured like the example 1, and the 1st 3OHo1 B-2C7 film was formed for the 1st 3OHo1 B-2C7 film with the heater temperature of 920 degrees C by the thickness of 1 micrometer like the example 1 on it. Then, the 2nd 3OHo1 B-2C7 film with a thickness of 1 micrometer was shaken like the example 1 on it with the heater temperature of 990 degrees C, 1000 degrees C, 1020 degrees C, 1030 degrees C, and 1040 degrees C, and membranes were formed.

[0045] Consequently, 3OHo1 B-2C7 film which has the property (electrization Jc) of 0.6 MA/cm<sup>2</sup> (77K, 0T) also by a maximum of 0.8 MA/cm<sup>2</sup> (77K, 0T) and average was obtained from the heater temperature of 990 degrees C among 1020 degrees C. In addition, at the time of these film formation, oxygen tension was considered as a part for 26.6Pa (= 200mTorr) and oxygen flow rate of 300cm<sup>3</sup>/s(= 300sccm).

[0046] As a comparison, as a result of forming 3OHo1 B-2C7 film of 0.8 micrometers of thickness on the 3 inch single crystal substrate of LaAlO<sub>3</sub> on the same conditions as 3OHo1 B-2C7 film of the upper layer of an example 2, it is checking that the film which has the property (electrization Jc) of 2 - 4.6 MA/cm<sup>2</sup> (77K, 0T) in a field 1000 degrees C or more is formed.

[0047] (Example 3) the field side of the silver tape of the tape substrate (width of face of 10mm) which made the silver tape with a thickness of 30 micrometers compound-ize on the tape which consists of stainless steel with a thickness of 70 micrometers — PLD — the 1st superconduction layer which consists of 3OHo1 B-2C7 film was formed by the thickness of 1 micrometer using law (laser vacuum deposition). The stacking tendency within a field was using what has the biaxial stacking tendency which is 16 degrees, and manufactured the silver tape which formed superconduction in one side of a tape substrate by the so-called Rabbits method. Membrane formation conditions were 900 degrees C in heater temperature at the time of a part for 13.3Pa (=100mTorr) of oxygen tension, and oxygen flow rate of 100cm<sup>3</sup>/s(=100sccm), laser

output 100W (1Jx100Hz), and membrane formation. The stacking tendency within a field of the 1st superconduction layer at this time was 14 degrees, and critical current density  $J_c$  was 0.3 MA/cm<sup>2</sup> (77K, 0T).

[0048] a 1st superconduction layer top -- further -- PLD -- the 2nd superconduction layer which consists of 3OHO1 B-2C7 film was formed by the thickness of 1 micrometer using law. Membrane formation conditions were 940 degrees C in heater temperature at the time of a part for 26.6Pa (=200mTorr) of oxygen tension, and oxygen flow rate of 100cm<sup>3</sup>/ (=100sccm), laser output 100W (1Jx100Hz), and membrane formation. The stacking tendency within a field of the 2nd superconduction layer at this time was 12 degrees. Although the measured critical current density  $J_c$  was 0.4 MA/cm<sup>2</sup> (77K, 0T), this critical current density  $J_c$  serves as the average of each critical current density  $J_c$  of the 1st superconduction layer and the 2nd superconduction layer, and the critical current density  $J_c$  of the parenchyma of the 2nd superconduction layer was presumed to be 0.6 MA/cm<sup>2</sup> (77K, 0T).

[0049] In this example, the interlayer is not used on the tape substrate. However, since silver is the construction material which a diffusion reaction with a superconduction layer cannot produce easily compared with other metal tapes (nickel, stainless steel, etc.), even if it vapor-deposits a superconduction layer at a direct elevated temperature on silver, the property of the good critical current density  $J_c$  is acquired. By forming a superconduction layer on such silver by the technique (that is, the technique of forming the 2nd superconduction layer on it by using the 1st superconduction layer as a diffusion prevention layer) of this invention, the thin film superconduction wire rod which has the property (that is, high critical current density  $J_c$ ) of the still better critical current density  $J_c$  was obtained.

[0050] It should be thought that the gestalt and example of operation which were indicated this time are [ no ] instantiation at points, and restrictive. The range of this invention is shown by the above-mentioned not explanation but claim, and it is meant that all modification in a claim, equal semantics, and within the limits is included.

[0051]

[Effect of the Invention] Since the 1st superconduction layer turns into a diffusion prevention layer according to the thin film superconduction wire rod and its manufacture approach of this invention as explained above, it can prevent that the metallic element of a metal tape substrate is spread in the 2nd superconduction layer. It can prevent by this that the 2nd superconduction layer carries out a diffusion reaction with a metal tape substrate, and the thin film superconduction wire rod which has high critical current density can be obtained.

[0052] Moreover, since the 1st superconduction layer used as a diffusion prevention layer turns into the 2nd superconduction layer from the same construction material substantially, a diffusion reaction does not arise between the 1st superconduction layer and the 2nd superconduction layer.

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DESCRIPTION OF DRAWINGS

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## [Brief Description of the Drawings]

[Drawing 1] It is the partial cross-section perspective view showing roughly the configuration of the thin film superconduction wire rod in the gestalt of 1 operation of this invention.

[Drawing 2] It is the partial cross-section perspective view showing roughly the configuration of the conventional thin film superconduction wire rod.

[Drawing 3] It is the partial cross-section perspective view showing roughly the configuration of the thin film superconduction wire rod which omitted the interlayer from the configuration of drawing 1 .

[Drawing 4] It is the partial cross-section perspective view showing roughly the configuration of the thin film superconduction wire rod which omitted the interlayer using the metal tape substrate which compound-ized the silver tape.

[Drawing 5] It is flow drawing showing the manufacture approach of the thin film superconduction wire rod in the gestalt of 1 operation of this invention.

## [Description of Notations]

1 A metal tape substrate, 2 An interlayer, 3 The 1st superconduction layer, 4 The 2nd superconduction layer, 5 A silver larer, 10A, 10B Thin film superconduction wire rod.

[Translation done.]

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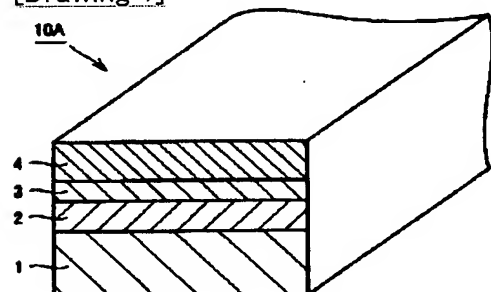
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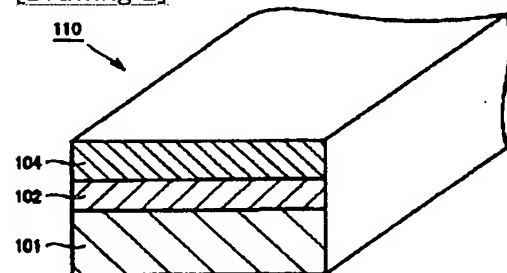
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## DRAWINGS

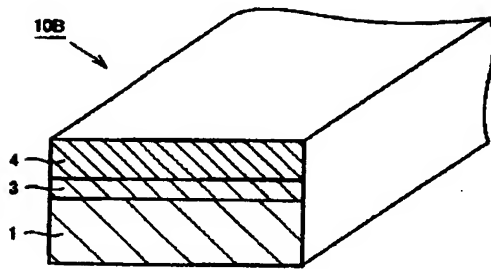
[Drawing 1]



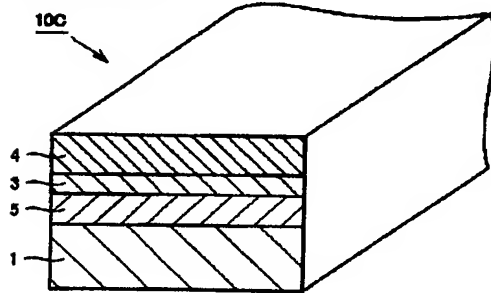
[Drawing 2]



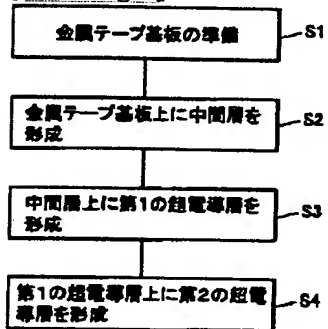
[Drawing 3]



[Drawing 4]



[Drawing 5]



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TECHNICAL FIELD

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[Field of the Invention] Especially this invention relates to the thin film superconduction wire rod with which the superconduction layer which has the presentation of RE123 system was formed on the metal tape substrate, and its manufacture approach about a thin film superconduction wire rod and its manufacture approach.

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[Translation done.]

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PRIOR ART

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[Description of the Prior Art] When forming a superconduction thin film of RE123 system like the presentation of RE1 B-2C 3O7 on a single crystal substrate, high critical current density ( $J_c$ ) is obtained, but when forming on a metal tape substrate, high critical current density is difficult to get. this -- a single crystal -- a substrate -- a case -- \*\*\*\* -- aluminum -- two -- O -- three -- LaAlO -- three -- MgO -- etc. -- an oxide -- a substrate -- using -- having -- a sake -- a substrate -- superconduction -- a thin film -- diffusion -- a reaction -- being generated -- being hard -- although -- a metal -- a tape -- a substrate -- a case -- \*\*\*\* -- a metal -- a tape -- a substrate -- using -- having -- stainless steel -- nickel -- (-- nickel --) -- an alloy -- silver -- (-- Ag --) -- an alloy -- etc. -- superconduction -- a thin film -- diffusion -- a reaction -- be generated -- since -- it is .

[0003] In addition, in the above ""RE" of RE1 B-2C3O7" is "B about rare earth elements (for example, yttrium)", "C" means copper (Cu) and "O" means oxygen (O) for barium (Ba).

[0004] Moreover, it improves, junction between crystal grain also becomes firm, and the compactness of the crystal of RE123 system can attain the high critical current density  $J_c$ , so that the temperature at the time of membrane formation by the gaseous-phase method (laser vacuum deposition, a spatter, electron beam method) is high. However, as for a metal tape substrate, the diffusion reaction of a substrate and a superconduction thin film serves as activity at an elevated temperature for a metal. For this reason, generally by the gaseous-phase method, temperature at the time of membrane formation was not able to be made into the elevated temperature.

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EFFECT OF THE INVENTION

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[Effect of the Invention] Since the 1st superconduction layer turns into a diffusion prevention layer according to the thin film superconduction wire rod and its manufacture approach of this invention as explained above, it can prevent that the metallic element of a metal tape substrate is spread in the 2nd superconduction layer. It can prevent by this that the 2nd superconduction layer carries out a diffusion reaction with a metal tape substrate, and the thin film superconduction wire rod which has high critical current density can be obtained.

[0052] Moreover, since the 1st superconduction layer used as a diffusion prevention layer turns into the 2nd superconduction layer from the same quality of the material substantially, a diffusion reaction does not arise between the 1st superconduction layer and the 2nd superconduction layer.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] In order to prevent the above-mentioned diffusion reaction, interlayers, such as cerium oxide (CeO<sub>2</sub>) and yttria stabilized zirconia (YSZ), are formed between a metal tape and a superconduction layer.

[0006] However, since an interlayer's selenium (Ce), an yttrium (Y), etc. react with the superconduction layer of RE123 system, even if it prepares an interlayer, high critical current density  $J_c$  like [ in the case of forming a superconduction layer on a single crystal substrate ] is not obtained.

[0007] So, the purpose of this invention is offering the thin film superconduction wire rod which has high critical current density in the configuration which forms the superconduction layer of RE123 system on a metal tape substrate, and its manufacture approach.

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MEANS

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[Means for Solving the Problem] The manufacture approach of the thin film superconduction wire rod of this invention is equipped with the process which forms the 1st superconduction layer which has the presentation of RE123 system on a metal tape substrate, and the process which forms the 2nd superconduction layer which has the presentation of RE123 system so that the 1st superconduction layer may be touched.

[0009] According to the manufacture approach of the thin film superconduction wire rod of this invention, since the 1st superconduction layer turns into a diffusion prevention layer, it can prevent that the metallic element of a metal tape substrate is spread in the 2nd superconduction layer. It can prevent by this that the 2nd superconduction layer carries out a diffusion reaction with a metal tape substrate, and high critical current density can be obtained.

[0010] Moreover, since the 1st superconduction layer used as a diffusion prevention layer turns into the 2nd superconduction layer from the same quality of the material substantially, a diffusion reaction does not arise between the 1st superconduction layer and the 2nd superconduction layer.

[0011] In addition, "RE123 system" in this application specification means that it is  $0.7 \leq x \leq 1.3$ ,  $1.7 \leq y \leq 2.3$ , and  $2.7 \leq z \leq 3.3$  in  $\text{RE}_x\text{Ba}_y\text{Cu}_z\text{O}_{7-d}$ . Moreover, RE of "RE123 system" means the quality of the material of rare earth elements and an yttrium element which contains either at least. Moreover, as rare earth elements, neodymium (Nd), a gadolinium (Gd), HORUMINIUMU (Ho), samarium (Sm), etc. are contained, for example.

[0012] In the manufacture approach of the above-mentioned thin film superconduction wire rod, it has further preferably the process which forms an interlayer between a metal tape substrate and the 1st superconduction layer.

[0013] Thus, since the 1st superconduction layer functions as a diffusion prevention layer even when an interlayer is prepared, it can prevent that the 2nd superconduction layer carries out a diffusion reaction with an interlayer, and high critical current density can be obtained.

[0014] In the manufacture approach of the above-mentioned thin film superconduction wire rod, the temperature at the time of membrane formation of the 2nd superconduction layer is higher than the temperature at the time of membrane formation of the 1st superconduction layer preferably.

[0015] By making low temperature at the time of membrane formation of the 1st superconduction layer, it can control that the 1st superconduction layer carries out a diffusion reaction with the substrate of a metal tape etc. Moreover, by making high temperature at the time of membrane formation of the 2nd superconduction layer, it improves, junction between crystal grain also becomes firm, and the compactness of the crystal of the 2nd superconduction layer of RE123 system can attain the high critical current density  $J_c$ . Thus, by controlling the temperature at the time of membrane formation of each class, the thin film superconduction wire rod which is a diffusion reaction and which has a high critical current value while being able to control can be obtained.

[0016] In the manufacture approach of the above-mentioned thin film superconduction wire rod, the oxygen tension at the time of membrane formation of the 2nd superconduction layer is higher than the oxygen tension at the time of membrane formation of the 1st superconduction layer preferably.

[0017] Usually, in the superconduction layer of RE123 system, since the melting point of a superconduction layer will become high if the oxygen tension at the time of membrane formation becomes high, it becomes possible to make temperature at the time of membrane formation into an elevated temperature. Since this is enabled to form the 2nd superconduction layer at an elevated temperature rather than the 1st superconduction layer, as mentioned above, the compactness of the crystal of the 2nd superconduction layer improves, junction between crystal grain also becomes firm, and the high critical current density  $J_c$  can be attained.

[0018] The thin film superconduction wire rod of this invention is equipped with a metal tape substrate, the 1st superconduction layer, and the 2nd superconduction layer. The 1st superconduction layer contains the component which is formed on a metal tape substrate, has the presentation of RE123 system, and is contained in the quality of the material of a substrate. The 2nd superconduction layer does not contain the component which is formed so that the 1st superconduction layer may be touched, and has the presentation of RE123 system, and is contained in the quality of the material of a substrate.

[0019] According to the thin film superconduction wire rod of this invention, since the 1st superconduction layer turns into a diffusion prevention layer, it can prevent that the metallic element of a metal tape substrate is spread in the 2nd superconduction layer. It can prevent by this that the 2nd superconduction layer carries out a diffusion reaction with a metal tape substrate, and high critical current density can be obtained.

[0020] Moreover, since the 1st superconduction layer used as a diffusion prevention layer turns into the 2nd superconduction layer from the same quality of the material substantially, a diffusion reaction does not arise between the 1st superconduction layer and the 2nd superconduction layer.

[0021] In the above-mentioned thin film superconduction wire rod, it has further preferably the interlayer formed between a metal tape substrate and the 1st superconduction layer.

[0022] Thus, since the 1st superconduction layer functions as a diffusion prevention layer even when an interlayer is prepared, it can prevent that the 2nd superconduction layer carries out a diffusion reaction with an interlayer, and high critical current density can be obtained.

[0023]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained based on drawing.

[0024] Drawing 1 is the partial cross-section perspective view showing roughly the configuration of the thin film superconduction wire rod in the gestalt of 1 operation of this invention. With reference to drawing 1, the thin film superconduction wire rod 10 in the gestalt of this operation has the metal tape substrate 1, an interlayer 2, the 1st superconduction layer 3, and the 2nd superconduction layer 4.

[0025] The metal tape substrate 1 consists of the quality of the material of stainless steel, a nickel alloy (for example, Hastelloy), a silver alloy, etc. An interlayer 2 is a diffusion prevention layer, for example, consists of the quality of the materials, such as cerium oxide, YSZ, magnesium oxide, an oxidization yttrium, an oxidization ytterbium, and a barium zirconia, and is formed on the metal tape substrate 1.

[0026] The 1st superconduction layer 3 is formed on the interlayer 2, including the component which has the presentation of RE123 system and is contained in the quality of the material of a substrate (interlayer 2). The 2nd superconduction layer 4 does not contain the component which is formed so that the 1st superconduction layer 3 may be touched, and has the presentation of RE123 system, and is contained in the quality of the material of a substrate (interlayer 2). The 1st and 2nd superconduction layers 3 and 4 consist of the quality of the material of the same presentation substantially, for example, consist of Ho1 B-2C 3O7.

[0027] As shown in drawing 2, the conventional thin film superconduction wire rod 110 has the metal tape substrate 101, the interlayer 102, and the superconduction layer 103. As compared with this conventional configuration, a superconduction layer consists of two-layer [ of the 1st and 2nd superconduction layers 3 and 4 ], and, as for the configuration of the gestalt of this operation, the 1st superconduction layers 3 differ in the point (that is, it prevents that the metallic element in an interlayer 2 is spread in the 2nd superconduction layer 4) of functioning as a diffusion prevention layer. Thereby, by thin film superconduction wire rod 10A of the gestalt of this operation, an interlayer's 2 metallic

element is not contained in the 2nd superconduction layer 4 to an interlayer's 102 metallic element having been contained in the superconduction layer 104 in the conventional thin film superconduction wire rod 110.

[0028] Although the configuration which formed the interlayer 2 in drawing 1 was explained, as shown in drawing 3, the interlayer was omitted, and the 1st superconduction layer 3 may be directly in contact with the front face of the metal tape substrate 1. In this configuration, since the 1st superconduction layer 3 functions as a diffusion prevention layer, the metallic element of the metal tape substrate 1 is not contained in the 2nd superconduction layer 4.

[0029] In addition, since the configuration of those other than this of thin film superconduction wire rod 10B shown in drawing 3 is almost the same as the configuration shown in drawing 1 mentioned above, the explanation is omitted.

[0030] Moreover, the interlayer 2 who shows drawing 1 may be omitted, and as shown in drawing 4, a metal tape substrate may be used as the compound tape substrate of the tape 1 which consists of stainless steel, and the tape 5 which consists of silver. Silver is the quality of the material which a diffusion reaction with a superconduction layer cannot produce easily rather than other metals. For this reason, even if it vapor-deposits the superconduction layers 3 and 4 at a direct elevated temperature on a silver larer 5, the property of the good critical current density  $J_c$  is acquired.

[0031] In addition, since the configuration of those other than this of thin film superconduction wire rod 10C shown in drawing 4 is almost the same as the configuration shown in drawing 1 mentioned above, it attaches the sign same about the same member, and omits the explanation.

[0032] Next, the manufacture approach of the thin film superconduction wire rod in the gestalt of this operation is explained. Drawing 5 is the flow Fig. showing the manufacture approach of the thin film superconduction wire rod in the gestalt of 1 operation of this invention. the interlayer 2 who the metal tape substrate 1 is prepared (step S1), and consists of YSZ on this metal tape substrate 1 with reference to drawing 1 and drawing 5 by the manufacture approach of the thin film superconduction wire rod of the gestalt this operation -- PLD (Pulsed Laser Deposition) -- ISD (Inclined Substrate Deposition) by law (laser vacuum deposition) -- it is formed of law (step S2). the 1st superconduction layer 3 which has the presentation (for example, Ho1 B-2C 3O7) of RE123 system on this interlayer 2 -- for example, PLD -- it is formed of law (step S3). the 2nd superconduction layer 4 which has the presentation (for example, Ho1 B-2C 3O7) of RE123 system on this 1st superconduction layer 3 -- for example, PLD -- it is formed of law (step S4) and thin film superconduction wire rod 10A is manufactured by performing after treatment.

[0033] In addition, when manufacturing thin film superconduction wire rod 10B shown in drawing 3, the above-mentioned interlayer's 2 formation process (step S2) is skipped. Moreover, when manufacturing thin film superconduction wire rod 10C shown in drawing 4, a metal tape substrate is prepared as a compound tape substrate of the tape 1 which consists of stainless steel, and the tape 5 which consists of silver, and an interlayer's 2 formation process (step S2) is skipped.

[0034] According to the gestalt of this operation, since the 1st superconduction layer 3 functions as a diffusion prevention layer, it can prevent that an interlayer's 2 (or metal tape substrate 1) metallic element is spread in the 2nd superconduction layer 4. It can prevent by this that the 2nd superconduction layer 4 carries out a diffusion reaction with an interlayer 2 (or metal tape substrate 1), and high critical current density can be obtained.

[0035] Moreover, since the 1st superconduction layer 3 used as a diffusion prevention layer turns into the 2nd superconduction layer 4 from the same quality of the material substantially, a diffusion reaction does not arise between the 1st superconduction layer 3 and the 2nd superconduction layer 4.

[0036] As for the temperature at the time of membrane formation of the 2nd superconduction layer 4, in the above-mentioned manufacture approach, it is desirable that it is higher than the temperature at the time of membrane formation of the 1st superconduction layer 3. Thus, by making low temperature at the time of membrane formation of the 1st superconduction layer 3, it can control that the 1st superconduction layer 3 carries out a diffusion reaction with an interlayer's 2 (or metal tape substrate 1) substrate. Moreover, by making high temperature at the time of membrane formation of the 2nd

superconduction layer 4, it improves, junction between crystal grain also becomes firm, and the compactness of the crystal of the 2nd superconduction layer 4 of RE123 system can attain the high critical current density  $J_c$ . Thus, by controlling the temperature at the time of membrane formation of each class, thin film superconduction wire rod 10A (or 10B) which is a diffusion reaction and which has a high critical current value while being able to control can be obtained.

[0037] As for the oxygen tension at the time of membrane formation of the 2nd superconduction layer 4, in the above-mentioned manufacture approach, it is desirable that it is higher than the oxygen tension at the time of membrane formation of the 1st superconduction layer 3. Usually, in the superconduction layer of RE123 system, since the melting point of a superconduction layer will become high if the oxygen tension at the time of membrane formation becomes high, it becomes possible to make temperature at the time of membrane formation into an elevated temperature. Since this is enabled to form the 2nd superconduction layer 4 at an elevated temperature rather than the 1st superconduction layer 3, as mentioned above, the compactness of the crystal of the 2nd superconduction layer 4 improves, junction between crystal grain also becomes firm, and the high critical current density  $J_c$  can be attained.

[0038] Moreover, since the 1st superconduction layer 3 functions as a diffusion prevention layer, it becomes possible to take the long membrane formation time amount of the 2nd superconduction layer 4, and thick-film-ization (high  $J_c$ ) of the 2nd superconduction layer 4 is attained.

[0039] Moreover, when formed of the technique (Rabits (Rolling-Assisted Biaxially Textured Substrates) the ISD method and law) from which an interlayer 2 does not become comparatively precise, it becomes easy to diffuse a metallic element in a superconduction layer. For this reason, a diffusion reaction can be more effectively prevented by combining the gestalt of this operation with such an interlayer.

[0040] Moreover, as for the 1st of RE123 system and the 2nd superconduction layer 3 and 4 in the gestalt of this operation, it is desirable that the stacking tendency within a field is all the c-axis orientation film 20 degrees or less. Moreover, even if the 1st superconduction layer 3 which functions as a diffusion prevention layer has neither a gap of a presentation nor a certain specific element, it can play a role.

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EXAMPLE

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[Example]

(Example 1) a nickel alloy tape (70 micrometers in Hastelloy, width-of-face [ of 10mm ], thickness) top -- PLD -- the YSZ interlayer with a thickness of 2 micrometers was formed by the ISD method using law (laser vacuum deposition). Although the nickel alloy tape was non-orientation, the YSZ interlayer had the biaxial orientation whose stacking tendency within a field is about 18 degrees according to the effectiveness of ISD. besides -- 3OHo1 B-2C7 film -- PLD -- membranes were formed by the thickness of 1 micrometer by law. Membrane formation conditions are a part for 13.3Pa (=100mTorr) of oxygen tension, and oxygen flow rate of 300cm<sup>3</sup>/s(=300sccm), and laser output 50W (1Jx50Hz), and shook the heater temperature at the time of membrane formation by 10-degree-C unit from 900 degrees C to 1000 degrees C. Consequently, the film with the property (electrization Jc) of a maximum of 0.08 MA/cm<sup>2</sup> (77K, 0T) was obtained with the heater temperature of 920 degrees C. In the heater temperature of 960 degrees C, the critical current values Jc were 0.07 MA/cm<sup>2</sup>.

[0042] On the other hand, the 1st 3OHo1 B-2C7 1-micrometer film was formed with the heater temperature of 900 degrees C on the same conditions. Then, heater temperature was changed on the still more nearly same conditions with 920 degrees C, 940 degrees C, 960 degrees C, and 980 degrees C, and the 2nd 3OHo1 B-2C7 1-micrometer film was formed on it. Consequently, in the heater temperature of 960 degrees C, 3OHo1 B-2C7 film with the property (electrization Jc) of 0.3 MA/cm<sup>2</sup> (77K, 0T) was obtained.

[0043] As a result of observing by SEM (Scanning Electron Microscope), the 2nd 3OHo1 B-2C7 upper film was a very precise smooth film surface compared with the 1st 3OHo1 B-2C7 lower layer film.

[0044] (Example 2) The nickel alloy tape and YSZ interlayer who become a substrate were manufactured like the example 1, and the 1st 3OHo1 B-2C7 film was formed for the 1st 3OHo1 B-2C7 film with the heater temperature of 920 degrees C by the thickness of 1 micrometer like the example 1 on it. Then, the 2nd 3OHo1 B-2C7 film with a thickness of 1 micrometer was shaken like the example 1 on it with the heater temperature of 990 degrees C, 1000 degrees C, 1020 degrees C, 1030 degrees C, and 1040 degrees C, and membranes were formed.

[0045] Consequently, 3OHo1 B-2C7 film which has the property (electrization Jc) of 0.6 MA/cm<sup>2</sup> (77K, 0T) also by a maximum of 0.8 MA/cm<sup>2</sup> (77K, 0T) and average was obtained from the heater temperature of 990 degrees C among 1020 degrees C. In addition, at the time of these film formation, oxygen tension was considered as a part for 26.6Pa (= 200mTorr) and oxygen flow rate of 300cm<sup>3</sup>/s(= 300sccm).

[0046] As a comparison, as a result of forming 3OHo1 B-2C7 film of 0.8 micrometers of thickness on the 3 inch single crystal substrate of LaAlO<sub>3</sub> on the same conditions as 3OHo1 B-2C7 film of the upper layer of an example 2, it is checking that the film which has the property (electrization Jc) of 2 - 4.6 MA/cm<sup>2</sup> (77K, 0T) in a field 1000 degrees C or more is formed.

[0047] (Example 3) the field side of the silver tape of the tape substrate (width of face of 10mm) which made the silver tape with a thickness of 30 micrometers compound-ize on the tape which consists of stainless steel with a thickness of 70 micrometers -- PLD -- the 1st superconduction layer which consists

of 3OHo1 B-2C7 film was formed by the thickness of 1 micrometer using law (laser vacuum deposition). The stacking tendency within a field was using what has the biaxial stacking tendency which is 16 degrees, and manufactured the silver tape which formed superconduction in one side of a tape substrate by the so-called Rabits method. Membrane formation conditions were 900 degrees C in heater temperature at the time of a part for 13.3Pa (=100mTorr) of oxygen tension, and oxygen flow rate of 100cm<sup>3</sup>/s(=100sccm), laser output 100W (1Jx100Hz), and membrane formation. The stacking tendency within a field of the 1st superconduction layer at this time was 14 degrees, and critical current density Jc was 0.3 MA/cm<sup>2</sup> (77K, 0T).

[0048] a 1st superconduction layer top -- further -- PLD -- the 2nd superconduction layer which consists of 3OHo1 B-2C7 film was formed by the thickness of 1 micrometer using law. Membrane formation conditions were 940 degrees C in heater temperature at the time of a part for 26.6Pa (=200mTorr) of oxygen tension, and oxygen flow rate of 100cm<sup>3</sup>/s(=100sccm), laser output 100W (1Jx100Hz), and membrane formation. The stacking tendency within a field of the 2nd superconduction layer at this time was 12 degrees. Although the measured critical current density Jc was 0.4 MA/cm<sup>2</sup> (77K, 0T), this critical current density Jc serves as the average of each critical current density Jc of the 1st superconduction layer and the 2nd superconduction layer, and the critical current density Jc of the parenchyma of the 2nd superconduction layer was presumed to be 0.6 MA/cm<sup>2</sup> (77K, 0T).

[0049] In this example, the interlayer is not used on the tape substrate. However, since silver is the quality of the material which a diffusion reaction with a superconduction layer cannot produce easily compared with other metal tapes (nickel, stainless steel, etc.), even if it vapor-deposits a superconduction layer at a direct elevated temperature on silver, the property of the good critical current density Jc is acquired. By forming a superconduction layer on such silver by the technique (that is, the technique of forming the 2nd superconduction layer on it by using the 1st superconduction layer as a diffusion prevention layer) of this invention, the thin film superconduction wire rod which has the property (that is, high critical current density Jc) of the still better critical current density Jc was obtained.

[0050] It should be thought that the gestalt and example of operation which were indicated this time are [ no ] instantiation at points, and restrictive. The range of this invention is shown by the above-mentioned not explanation but claim, and it is meant that all modification in a claim, equal semantics, and within the limits is included.

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[Translation done.]



(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開2003-323822

(P2003-323822A)

(43) 公開日 平成15年11月14日 (2003. 11. 14)

(51) Int. CL <sup>7</sup>	識別記号	F I	テームコード (参考)
H 0 1 B 12/06		H 0 1 B 12/06	4 K 0 2 9
13/00	5 6 5	13/00	5 6 5 D 5 G 3 2 1
/ C 2 3 C 14/06		C 2 3 C 14/06	S

審査請求 未請求 請求項の数 6 O L (全 6 頁)

(21) 出願番号 特願2002-130623 (P2002-130623)

(22) 出願日 平成14年5月2日 (2002. 5. 2)

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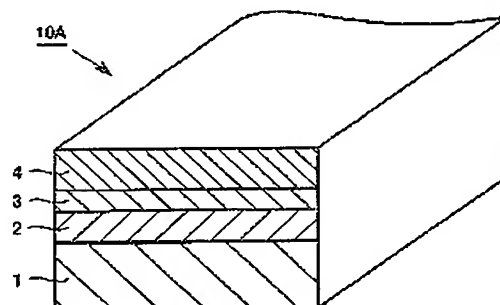
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(54) 【発明の名称】 薄膜超電導線材およびその製造方法

(57) 【要約】

【課題】 金属テープ基板上に R E 1 2 3 系の超電導層を形成する構成において高い臨界電流密度を有する薄膜超電導線材およびその製造方法を提供する。

【解決手段】 本発明の薄膜超電導線材 1 0 A の製造方法は、金属テープ基板 1 上に中間層 2 を形成する工程と、その中間層 2 上に R E 1 2 3 系の組成を有する第 1 の超電導層 3 を並敵防止層として形成する工程と、第 1 の超電導層 3 に接するように、R E 1 2 3 系の組成を有する第 2 の超電導層 4 を形成する工程とを備えている。



(2)

特開2003-323822

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## 【特許請求の範囲】

【請求項1】 金属テープ基板上にRE123系の組成を有する第1の超電導層を形成する工程と、前記第1の超電導層に接するように、RE123系の組成を有する第2の超電導層を形成する工程とを備えた、薄膜超電導線材の製造方法。

【請求項2】 前記金属テープ基板と前記第1の超電導層との間に中間層を形成する工程をさらに備えたことを特徴とする、請求項1に記載の薄膜超電導線材の製造方法。

【請求項3】 前記第2の超電導層の成膜時の温度は、前記第1の超電導層の成膜時の温度よりも高いことを特徴とする、請求項1または2に記載の薄膜超電導線材の製造方法。

【請求項4】 前記第2の超電導層の成膜時の酸素分圧は、前記第1の超電導層の成膜時の酸素分圧よりも高いことを特徴とする、請求項3に記載の薄膜超電導線材の製造方法。

【請求項5】 金属テープ基板と、前記金属テープ基板上に形成され、かつRE123系の組成を有し、かつ下地の材質に含まれる成分を含む第1の超電導層と、

前記第1の超電導層に接するように形成され、かつRE123系の組成を有し、かつ前記下地の材質に含まれる成分を含まない第2の超電導層とを備えた、薄膜超電導線材。

【請求項6】 前記金属テープ基板と前記第1の超電導層との間に形成された中間層をさらに備えたことを特徴とする、請求項5に記載の薄膜超電導線材。

## 【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、薄膜超電導線材およびその製造方法に関し、特に、RE123系の組成を有する超電導層が金属テープ基板上に形成された薄膜超電導線材およびその製造方法に関するものである。

【0002】

【従来の技術】RE、B、C、O<sub>2</sub>の組成のようなRE123系の超電導薄膜を、単結晶基板上に形成する場合には高い臨界電流密度(J<sub>c</sub>)が得られるが、金属テープ基板上に形成する場合には高い臨界電流密度が得難い。これは、単結晶基板の場合にはAl<sub>2</sub>O<sub>3</sub>、LaAlO<sub>3</sub>、MgOなどの酸化物基板が用いられるため基板と超電導薄膜との拡散反応が生じ難いが、金属テープ基板の場合には金属テープ基板に用いられるステンレス、ニッケル(Ni)合金、銀(Ag)合金などと超電導薄膜との拡散反応が生じてしまうからである。

【0003】なお、上記「RE、B、C、O<sub>2</sub>」の「RE」は希土類元素(たとえばイットリウム)を、「B」はバリウム(Ba)を、「C」は銅(Cu)を、「O」は酸素(O)を意味している。

【0004】また、気相法(レーザ蒸着法、スパッタ法、電子ビーム法)による成膜時の温度が高いほど、RE123系の結晶の緻密性は向上し、結晶粒間の接合も強固になり、高い臨界電流密度J<sub>c</sub>が達成できる。ただし、金属テープ基板は金属のため、基板と超電導薄膜との拡散反応が高温で活性となる。このため、一般に気相法では、成膜時の温度を高温にすることができなかった。

【0005】

10 【発明が解決しようとする課題】上記の拡散反応を防止するため、酸化セリウム(CeO<sub>2</sub>)、イットリア安定化ジルコニア(YSZ)などの中間層が金属テープと超電導層との間に形成される。

【0006】しかしながら、中間層のセレン(Ce)、イットリウム(Y)などもRE123系の超電導層と反応してしまうので、中間層を設けても単結晶基板上に超電導層を形成する場合のような高い臨界電流密度J<sub>c</sub>は得られない。

【0007】それゆえ本発明の目的は、金属テープ基板上にRE123系の超電導層を形成する構成において高い臨界電流密度を有する薄膜超電導線材およびその製造方法を提供することである。

【0008】

【課題を解決するための手段】本発明の薄膜超電導線材の製造方法は、金属テープ基板上にRE123系の組成を有する第1の超電導層を形成する工程と、第1の超電導層に接するように、RE123系の組成を有する第2の超電導層を形成する工程とを備えている。

30 【0009】本発明の薄膜超電導線材の製造方法によれば、第1の超電導層が拡散防止層となるため、第2の超電導層に金属テープ基板の金属元素が拡散することを防止することができる。これにより、第2の超電導層が金属テープ基板と拡散反応することが防止でき、高い臨界電流密度を得ることができる。

【0010】また拡散防止層となる第1の超電導層が第2の超電導層と実質的に同一の材質よりなるため、第1の超電導層と第2の超電導層との間で拡散反応が生じることもない。

40 【0011】なお、本願明細書における「RE123系」とは、RE<sub>x</sub>Ba<sub>y</sub>Cu<sub>z</sub>O<sub>w</sub>において、0.7 ≤ x ≤ 1.3、1.7 ≤ y ≤ 2.3、2.7 ≤ z ≤ 3.3であることを意味する。また、「RE123系」のREは、希土類元素およびイットリウム元素の少なくともいずれかを含む材質を意味する。また、希土類元素としては、たとえばネオジム(Nd)、ガドリニウム(Gd)、ホルミウム(Ho)、サマリウム(Sm)などが含まれる。

50 【0012】上記の薄膜超電導線材の製造方法において好ましくは、金属テープ基板と第1の超電導層との間に中間層を形成する工程がさらに備えられている。

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【0013】このように中間層を設けた場合でも、第1の超電導層が拡散防止層として機能するため、第2の超電導層が中間層と拡散反応することが防止でき、高い臨界電流密度を得ることができる。

【0014】上記の薄膜超電導線材の製造方法において好ましくは、第2の超電導層の成膜時の温度は、第1の超電導層の成膜時の温度よりも高い。

【0015】第1の超電導層の成膜時の温度を低くすることにより、第1の超電導層が金属テープなどの下地と拡散反応することを抑制することができる。また、第2の超電導層の成膜時の温度を高くすることにより、RE123系の第2の超電導層の結晶の緻密性は向上し、結晶粒間の接合も強固になり、高い臨界電流密度Jcを達成することができる。このように各層の成膜時の温度を制御することにより、拡散反応の抑制できるとともに高い臨界電流値を有する薄膜超電導線材を得ることができる。

【0016】上記の薄膜超電導線材の製造方法において好ましくは、第2の超電導層の成膜時の酸素分圧は、第1の超電導層の成膜時の酸素分圧よりも高い。

【0017】通常、RE123系の超電導層では成膜時の酸素分圧が高くなると超電導層の融点が高くなるため、成膜時の温度を高温にすることが可能となる。これにより第2の超電導層を第1の超電導層よりも高温で成膜することが可能となるため、上述したように第2の超電導層の結晶の緻密性が向上し、結晶粒間の接合も強固になり、高い臨界電流密度Jcを達成することができる。

【0018】本発明の薄膜超電導線材は、金属テープ基板と、第1の超電導層と、第2の超電導層とを備えている。第1の超電導層は、金属テープ基板上に形成され、かつRE123系の組成を有し、かつ下地の材質に含まれる成分を含む。第2の超電導層は、第1の超電導層に接するように形成され、かつRE123系の組成を有し、かつ下地の材質に含まれる成分を含まない。

【0019】本発明の薄膜超電導線材によれば、第1の超電導層が拡散防止層となるため、第2の超電導層に金属テープ基板の金属元素が拡散することを防止することができる。これにより、第2の超電導層が金属テープ基板と拡散反応することが防止でき、高い臨界電流密度を得ることができる。

【0020】また拡散防止層となる第1の超電導層が第2の超電導層と実質的に同一の材質よりなるため、第1の超電導層と第2の超電導層との間で拡散反応が生じることもない。

【0021】上記の薄膜超電導線材において好ましくは、金属テープ基板と第1の超電導層との間に形成された中間層がさらに備えられている。

【0022】このように中間層を設けた場合でも、第1の超電導層が拡散防止層として機能するため、第2の超

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電導層が中間層と拡散反応することが防止でき、高い臨界電流密度を得ることができる。

【0023】

【発明の実施の形態】以下、本発明の実施の形態について図に基づいて説明する。

【0024】図1は、本発明の一実施の形態における薄膜超電導線材の構成を概略的に示す部分断面斜視図である。図1を参照して、本実施の形態における薄膜超電導線材10は、金属テープ基板1と、中間層2と、第1の超電導層3と、第2の超電導層4とを有している。

【0025】金属テープ基板1は、たとえばステンレス、ニッケル合金（たとえばハステロイ）、銀合金などの材質からなっている。中間層2は、拡散防止層であり、たとえば酸化セリウム、YSZ、酸化マグネシウム、酸化イットリウム、酸化イットルビウム、バリウムジルコニアなどの材質からなっており、金属テープ基板1上に形成されている。

【0026】第1の超電導層3は、RE123系の組成を有し、かつ下地（中間層2）の材質に含まれる成分を含み、かつ中間層2上に形成されている。第2の超電導層4は、第1の超電導層3に接するように形成され、かつRE123系の組成を有し、かつ下地（中間層2）の材質に含まれる成分を含まない。第1および第2の超電導層3、4は、実質的に同じ組成の材質よりなり、たとえばHf、B、C、Oよりなっている。

【0027】図2に示すように従来の薄膜超電導線材110は、金属テープ基板101と、中間層102と、超電導層103とを有している。この従来の構成と比較すると、本実施の形態の構成は、超電導層が第1および第2の超電導層3、4の2層よりなり、第1の超電導層3が拡散防止層として機能する（つまり中間層2内の金属元素が第2の超電導層4に拡散するのを防止する）点において異なる。これにより、従来の薄膜超電導線材110では超電導層104に中間層102の金属元素が含まれていたのに対し、本実施の形態の薄膜超電導線材10Aでは第2の超電導層4には中間層2の金属元素が含まれていない。

【0028】図1においては中間層2を設けた構成について説明したが、図3に示すように中間層が省略されて、第1の超電導層3が金属テープ基板1の表面に直接接していてもよい。この構成においても、第1の超電導層3が拡散防止層として機能するため、第2の超電導層4には金属テープ基板1の金属元素が含まれていない。

【0029】なお、図3に示す薄膜超電導線材10Bのこれ以外の構成は、上述した図1に示す構成とはほぼ同じであるため、その説明を省略する。

【0030】また、図1に示す中間層2が省略され、図4に示すように金属テープ基板がたとえばステンレスよりなるテープ1と銀よりなるテープ5との複合テープ基板とされてもよい。銀は、他の金属よりも超電導層との

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拡散反応の生じにくい材質である。このため、超電導層3、4を銀層5上に直接高温で蒸着しても良好な臨界電流密度 $J_c$ の特性が得られる。

【0031】なお、図4に示す薄膜超電導線材10Cのこれ以外の構成は、上述した図1に示す構成とはほぼ同じであるため、同一の部材については同一の符号を付し、その説明を省略する。

【0032】次に、本実施の形態における薄膜超電導線材の製造方法について説明する。図5は、本発明の一実施の形態における薄膜超電導線材の製造方法を示すフロー図である。図1および図5を参照して、本実施の形態の薄膜超電導線材の製造方法では、金属テープ基板1が準備され（ステップS1）、この金属テープ基板1上にたとえばYSZよりなる中間層2がPLD（Pulsed Laser Deposition）法（レーザ蒸着法）によるISD（Inclined Substrate Deposition）法により形成される（ステップS2）。この中間層2上に、RE123系の組成（たとえば $HfO_2B_2C_2O_7$ ）を有する第1の超電導層3がたとえばPLD法により形成される（ステップS3）。この第1の超電導層3上に、RE123系の組成（たとえば $HfO_2B_2C_2O_7$ ）を有する第2の超電導層4がたとえばPLD法により形成され（ステップS4）、後処理を施すことにより薄膜超電導線材10Aが製造される。

【0033】なお、図3に示す薄膜超電導線材10Bを製造するときには、上記の中間層2の形成工程（ステップS2）が省略される。また、図4に示す薄膜超電導線材10Cを製造するときには、金属テープ基板がたとえばステンレスよりなるテープ1と銀よりなるテープ5との接合テープ基板として準備され、中間層2の形成工程（ステップS2）が省略される。

【0034】本実施の形態によれば、第1の超電導層3が拡散防止層として機能するため、第2の超電導層4に中間層2（または金属テープ基板1）の金属元素が拡散することを防止することができる。これにより、第2の超電導層4が中間層2（または金属テープ基板1）と拡散反応することが防止でき、高い臨界電流密度を得ることができる。

【0035】また拡散防止層となる第1の超電導層3が第2の超電導層4と実質的に同一の材質よりなるため、第1の超電導層3と第2の超電導層4との間で拡散反応が生じることもない。

【0036】上記の製造方法においては、第2の超電導層4の成膜時の温度は、第1の超電導層3の成膜時の温度よりも高いことが好ましい。このように第1の超電導層3の成膜時の温度を低くすることにより、第1の超電導層3が中間層2（または金属テープ基板1）の下地と拡散反応することを抑制することができる。また、第2の超電導層4の成膜時の温度を高くすることにより、RE123系の第2の超電導層4の結晶の緻密性は向上

し、結晶粒間の接合も強固になり、高い臨界電流密度 $J_c$ を達成することができる。このように各層の成膜時の温度を制御することにより、拡散反応の抑制できるとともに高い臨界電流値を有する薄膜超電導線材10A（または10B）を得ることができる。

【0037】上記の製造方法においては、第2の超電導層4の成膜時の酸素分圧は、第1の超電導層3の成膜時の酸素分圧よりも高いことが好ましい。通常、RE123系の超電導層では成膜時の酸素分圧が高くなると超電導層の融点が高くなるため、成膜時の温度を高温にすることが可能となる。これにより第2の超電導層4を第1の超電導層3よりも高温で成膜することが可能となるため、上述したように第2の超電導層4の結晶の緻密性が向上し、結晶粒間の接合も強固になり、高い臨界電流密度 $J_c$ を達成することができる。

【0038】また、第1の超電導層3が拡散防止層として機能するため、第2の超電導層4の成膜時間を長くすることが可能となり、第2の超電導層4の厚膜化（高 $J_c$ ）が可能となる。

【0039】また中間層2が比較的緻密とならない手法（ISD法やRolling-Assisted Biaxially Textured Substrates）法により形成された場合には、金属元素が超電導層に拡散しやすくなる。このため、このような中間層に本実施の形態を組み合わせることで、より効果的に拡散反応を防止することができる。

【0040】また本実施の形態におけるRE123系の第1および第2の超電導層3、4はいずれも面内配向性が $20^\circ$ 以下のc軸配向膜であることが好ましい。また、拡散防止層として機能する第1の超電導層3は、組成のずれや、ある特定の元素がなくても役割を果たすことができる。

【0041】

【実施例】

（実施例1）ニッケル合金テープ（ハステロイ、幅10mm、厚さ70 $\mu$ m）の上にPLD法（レーザ蒸着法）を用いてISD法で厚さ2 $\mu$ mのYSZ中間層を成膜した。ニッケル合金テープは無配向であるが、YSZ中間層はISDの効果により面内配向性が約 $18^\circ$ の2軸配向を有していた。この上に、 $HfO_2B_2C_2O_7$ 膜をPLD法により1 $\mu$ mの厚さで成膜した。成膜条件は、酸素分圧13.3Pa（=100mTorr）、酸素流量300 $cm^3$ /分（=300sccm）、レーザ出力50W（1J $\times$ 50Hz）であり、成膜時のヒータ温度を900 $^\circ$ Cから1000 $^\circ$ Cまで10 $^\circ$ C刻みで振った。その結果、最高で0.08MA/ $cm^2$ （77K、0T）の特性（通電法 $J_c$ ）を持つ膜がヒータ温度920 $^\circ$ Cで得られた。ヒータ温度960 $^\circ$ Cでは臨界電流値 $J_c$ は0.07MA/ $cm^2$ であった。

【0042】一方、同様な条件でヒータ温度900 $^\circ$ Cにて1 $\mu$ mの第1の $HfO_2B_2C_2O_7$ 膜を成膜した。その

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後、さらに同様な条件でヒータ温度を920℃、940℃、960℃、980℃と変えてその上に1μmの第2のH<sub>o</sub>,B<sub>2</sub>C<sub>3</sub>O<sub>7</sub>膜を成膜した。その結果、ヒータ温度960℃において、0.3MA/cm<sup>2</sup>(77K、0T)の特性(通電法J<sub>c</sub>)を持つH<sub>o</sub>,B<sub>2</sub>C<sub>3</sub>O<sub>7</sub>膜が得られた。

【0043】SEM(Scanning Electron Microscope)で観察した結果、上層の第2のH<sub>o</sub>,B<sub>2</sub>C<sub>3</sub>O<sub>7</sub>膜は下層の第1のH<sub>o</sub>,B<sub>2</sub>C<sub>3</sub>O<sub>7</sub>膜に比べて、非常に緻密な平滑な膜面であった。

【0044】(実施例2)下地となるニッケル合金テープおよびYSZ中間層を実施例1と同様に製造し、その上に第1のH<sub>o</sub>,B<sub>2</sub>C<sub>3</sub>O<sub>7</sub>膜を実施例1と同様に1μmの厚さでヒータ温度920℃にて第1のH<sub>o</sub>,B<sub>2</sub>C<sub>3</sub>O<sub>7</sub>膜を成膜した。その後、その上に実施例1と同様に1μmの厚みの第2のH<sub>o</sub>,B<sub>2</sub>C<sub>3</sub>O<sub>7</sub>膜をヒータ温度990℃、1000℃、1020℃、1030℃、1040℃と振って成膜した。

【0045】その結果、最高で0.8MA/cm<sup>2</sup>(77K、0T)、平均でも0.6MA/cm<sup>2</sup>(77K、0T)の特性(通電法J<sub>c</sub>)を有するH<sub>o</sub>,B<sub>2</sub>C<sub>3</sub>O<sub>7</sub>膜がヒータ温度990℃から1020℃の間で得られた。なお、これらの膜形成時には酸素分圧を26.6Pa(=200mTorr)、酸素流量300cm<sup>3</sup>/分(=300sccm)とした。

【0046】比較として、LaAlO<sub>3</sub>の3インチ単結晶基板上に膜厚0.8μmのH<sub>o</sub>,B<sub>2</sub>C<sub>3</sub>O<sub>7</sub>膜を実施例2の上層のH<sub>o</sub>,B<sub>2</sub>C<sub>3</sub>O<sub>7</sub>膜と同一条件で成膜した結果、1000℃以上の領域で2~4.6MA/cm<sup>2</sup>(77K、0T)の特性(通電法J<sub>c</sub>)を有する膜が形成されることを確認している。

【0047】(実施例3)厚さ70μmのステンレスよりなるテープ上に、厚さ30μmの銀テープを複合化させたテープ基板(幅10mm)の銀テープの面側にPLD法(レーザ蒸着法)を用いて、H<sub>o</sub>,B<sub>2</sub>C<sub>3</sub>O<sub>7</sub>膜よりなる第1の超電導層を1μmの厚さで成膜した。テープ基板の片側に超電導を成膜した銀テープは面内配向性が16°の2軸配向性を有するものを使用しており、いわゆるRabits法で製作した。成膜条件は、酸素分圧13.3Pa(=100mTorr)、酸素流量100cm<sup>3</sup>/分(=100sccm)、レーザ出力100W(1J×100Hz)、成膜時のヒータ温度900℃であった。このときの第1の超電導層の面内配向性は14°、臨界電流密度J<sub>c</sub>は0.3MA/cm<sup>2</sup>(77K、0T)であった。

【0048】第1の超電導層上にさらにPLD法を用いて、H<sub>o</sub>,B<sub>2</sub>C<sub>3</sub>O<sub>7</sub>膜よりなる第2の超電導層を1μmの厚さで成膜した。成膜条件は、酸素分圧26.6Pa(=200mTorr)、酸素流量100cm<sup>3</sup>/分(=100sccm)、レーザ出力100W(1J×1

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00Hz)、成膜時のヒータ温度940℃であった。このときの第2の超電導層の面内配向性は12°であった。測定した臨界電流密度J<sub>c</sub>は0.4MA/cm<sup>2</sup>(77K、0T)であったが、この臨界電流密度J<sub>c</sub>は第1の超電導層と第2の超電導層との各臨界電流密度J<sub>c</sub>の平均値となっており、第2の超電導層の実質的な臨界電流密度J<sub>c</sub>は0.6MA/cm<sup>2</sup>(77K、0T)と推定された。

【0049】本実施例では、テープ基板上に中間層が用いられていない。しかし、銀は超電導層との拡散反応が他の金属テープ(ニッケル、ステンレスなど)に比べて生じにくい材質であるため、超電導層を銀上に直接高温で蒸着しても良好な臨界電流密度J<sub>c</sub>の特性が得られる。このような銀上に本発明の手法(つまり第1の超電導層を拡散防止層として、その上に第2の超電導層を形成する手法)で超電導層を形成することにより、さらに良好な臨界電流密度J<sub>c</sub>の特性(つまり高い臨界電流密度J<sub>c</sub>)を有する薄膜超電導線材が得られた。

【0050】今回開示された実施の形態および実施例はすべての点で例示であって制限的なものではないと考えられるべきである。本発明の範囲は上記した説明ではなくて特許請求の範囲によって示され、特許請求の範囲と均等の意味および範囲内でのすべての変更が含まれることが意図される。

【0051】

【発明の効果】以上説明したように本発明の薄膜超電導線材およびその製造方法によれば、第1の超電導層が拡散防止層となるため、第2の超電導層に金属テープ基板の金属元素が拡散することを防止することができる。これにより、第2の超電導層が金属テープ基板と拡散反応することが防止でき、高い臨界電流密度を有する薄膜超電導線材を得ることができる。

【0052】また拡散防止層となる第1の超電導層が第2の超電導層と実質的に同一の材質よりなるため、第1の超電導層と第2の超電導層との間で拡散反応が生じることもない。

【図面の簡単な説明】

【図1】 本発明の一実施の形態における薄膜超電導線材の構成を概略的に示す部分断面斜視図である。

【図2】 従来の薄膜超電導線材の構成を概略的に示す部分断面斜視図である。

【図3】 図1の構成から中間層を省略した薄膜超電導線材の構成を概略的に示す部分断面斜視図である。

【図4】 銀テープを複合化した金属テープ基板を用い、中間層を省略した薄膜超電導線材の構成を概略的に示す部分断面斜視図である。

【図5】 本発明の一実施の形態における薄膜超電導線材の製造方法を示すフロー図である。

【符号の説明】

1 金属テープ基板、2 中間層、3 第1の超電導

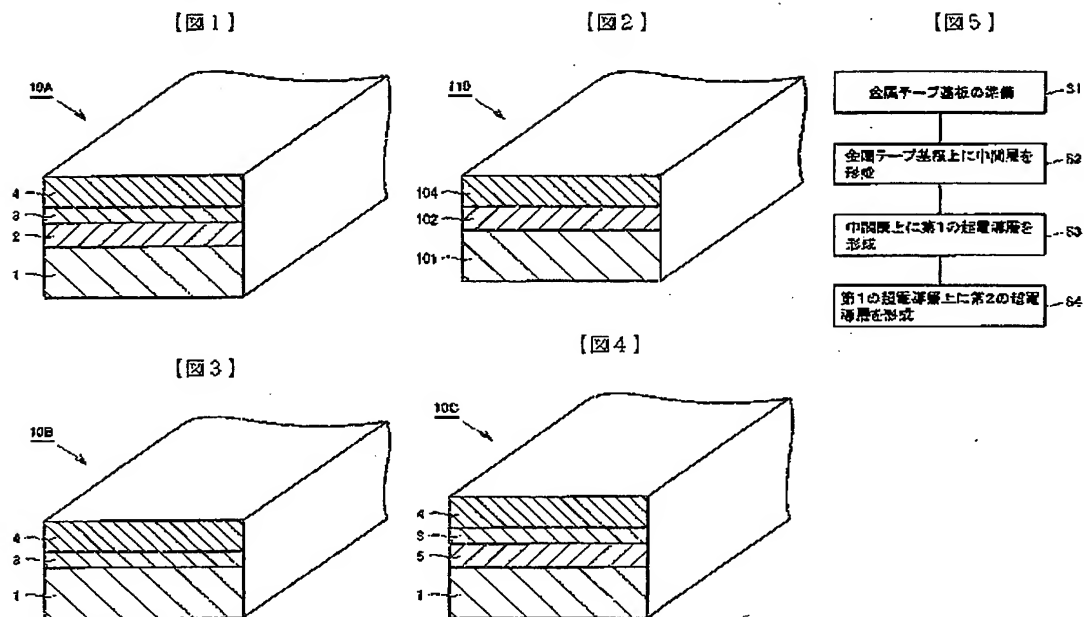
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図 4 第2の超電導層 5 銀層 10A, 10B \* \* 薄積超電導線材。



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Fターム(参考) 4K029 AA02 AA25 BA02 BA08 BB02  
BC04 CA01  
5G321 AA02 AA04 CA21 CA24 CA27  
CA28 CA38 DB36 DB37 DB39  
DB47